

REMARKS

Claims 4-5, 7-14, and 39-50 are in the application.

The claims have been amended by adding claims relating to the control of the porosity of the inert mineral particles by selection of the shape of the stone dust (claims 46 and 48), by the particle size distribution of the stone dust (claims 47 and 49), and by the ratio of stone dust to aluminosilicate binder material (claim 50). The new claims are fully supported by the application as filed, and in particular, by the specification at page 8, lines 21-29. No new matter is added thereby.

Applicants gratefully note that the Examiner has accepted applicants' request for continued examination and withdrawn the finality of the previous Office Action, and entered applicants' amendments to the claims.

Applicants gratefully acknowledge that the Examiner has withdrawn the objection to claim 17 on the ground that claim 17 was the substantial duplication of claim 8 in light of the applicants' amendments.

Applicants also gratefully acknowledge that the Examiner has withdrawn the provisional rejection of claims 1, 5-8, 16-17 under the judicially created doctrine of double patenting over claims 1-12, 21, and 25 of copending Application No. 10/600,847, in light of the applicants' amendments.

Further, applicants gratefully acknowledge that (1) the rejection of claims 1, 5, 7, 8, 13, and 14 as being anticipated by U.S. Patent 6,214,466 ("Joedicke"), (2) the rejection of claims 1, 5, 7, and 8 as being anticipated by U.S. Patent 3,528,842 ("Skadulis"), and (3) the rejection of claims 1, 5, 7 and 8 as being anticipated by U.S. Patent 3,507,676 ("McMahon"), have been withdrawn in view of applicants' amendments.

Claims 4, 5, 7, 8, 13, 14 and 39-43 stand rejected under 35 U.S.C. 103(a) as being unpatentable over U.S. Patent 5,022,897 ("Balcar et al.") in view of Joedicke or Skadulis or McMahon. This rejection is respectfully traversed, and reconsideration and withdrawal of the rejection as applicable to the amended claims are respectfully requested.

The Examiner states that Balcar et al. disclose a process for producing roofing granules (referencing column 6, line 16), the process comprising preparing base particles from a mixture including glass dust, which is a common byproduct in the manufacture of various glass articles (which the Examiner identifies with the "stone dust" in applicants' claims) such as soda/lime dust and high alumina soda/lime dust (referencing column 3, lines 40-48; column 4, lines 5-21; column 7, lines 25-28) and a sodium silicate or a similar substance (which the Examiner identifies with the "binder" in applicants' claims, and referencing column 5, lines 51-52) in a liquid form (referencing column 6, lines 4-7; column 8, lines 24-26) in an amount of 10 wt % (referencing column 7, lines 23-24) to pelletize the dusts (referencing column 8, line 26) followed by heating the mixture to 1200 °C to achieve fusion (referencing column 7, lines 33-36).

The Examiner further states that the prepared granules are insoluble and have many of the characteristics of soda lime glass with high alumina content (referencing column 6, lines 21-25). The Examiner notes that the mixture maybe passed through a simple extrusion system to compact it into a rod which is then directed into a dryer and ground as illustrated by the box 25 in Figure 2 (referencing column 6, lines 6-9). The Examiner further states that the melted material may be fritted for sale and subsequent reuse (referencing column 6, lines 10-11).

The Examiner acknowledges that the leachables from the frit (which the Examiner identifies with the presently claimed porous inert base particles) would meet current EPA standards for drinking water (referencing column 6, lines 11-12).

The Examiner states that it is her position that a kiln is conventionally used for heating to temperatures of 1200 °C.

The Examiner also takes the position that the prepared roofing granules have porosity within claimed range because they are prepared by a process substantially identical to that of claimed invention.

The Examiner further acknowledges that Balcar et al. fail to teach that providing at least one inorganic algacide on the base particles (as required by claim 39); and the binder being aluminosilicate (as required by claims 40, 44).

The Examiner states that Joedicke/Skadulis/McMahon teach that coating mineral base particles with a composition comprising zinc oxide, or zinc sulfide or cuprous oxide, kaolin (which the Examiner identifies with the claimed aluminosilicate) and sodium aqueous silicate, followed by firing the coating to insolubilize the coating, provides the mineral base particles with algae-resistance (referencing paragraphs 6-8 of the Office Action mailed on 8/10/2005).

The Examiner concludes that it would have been obvious to one of ordinary skill in the art at the time the invention was made to have coated roofing mineral particles of Balcar et al. with a composition comprising zinc oxide, or zinc sulfide or cuprous oxide, kaolin (which the Examiner identifies with the claimed aluminosilicate) and sodium aqueous silicate followed by firing the coating to insolubilize the coating with the expectation of providing the desired algae resistant roofing particles, as taught by Joedicke/Skadulis/McMahon.

The Examiner further states that as to claims 13-14, Joedicke and Skadulis teach the claimed limitations (referencing paragraphs 6 and 12 of the Office Action mailed on 8/10/2005).

In addition, the Examiner states that as to claim 40, as was discussed above, Balcar et al teach that a sodium silicate or a similar substance can be used a binder (referencing column 5, lines 51-52). The Examiner opines that, obviously a combination of a sodium silicate and a similar substance can be used a binder. The Examiner further notes that it is held that it is *prima facie* obvious to combine two compositions each of which is taught by the prior art to be useful for the same purpose, in order to form a third composition which is to be used for the very same purpose.

The Examiner further states that Balcar et al. further teach that alumina in a glass material provides a glass which exhibits good hardness with a less reactive surface (referencing column 4, lines 9-11). The Examiner notes that alumina is provided with the crusher dust (referencing column 7, lines 26-27). The Examiner also acknowledges that Balcar et al. fail to teach that the high content of alumina may provided using aluminosilicate.

The Examiner states that Joedicke/Skadulis/McMahon teach that sodium silicate may be used together with kaolin (aluminosilicate) to form a hard material after firing for forming roofing granules.

The Examiner further concludes that it would have been obvious to one of ordinary skill in the art at the time the invention was made to have used sodium silicate together with kaolin (aluminosilicate) in Balcar et al. with the expectation of providing the desired high alumina content since Joedicke/Skadulis/McMahon teach that sodium silicate may be used together with kaolin (aluminosilicate) to form a hard material after

firing for forming roofing granules, and Balcar et al. teach that a substance similar to sodium silicate can be used as a binder.

Applicants respectfully traverse the Examiner's conclusions, as they are based on an incorrect interpretation of Balcar et al.'s process. The Examiner takes the position that Balcar et al.'s process is substantially identical to applicants' process. This is not correct.

The Examiner identifies the glass dust in Balcar et al. with the stone chips in the presently claimed process. However, in Balcar et al.'s process, the glass dust is fused, that is, liquefied. The presently claimed process does not include a step requiring the stone chips to be fused. The process are not "substantially identical," or for that matter, even remotely similar. The products resulting from the processes have very different properties.

The "waste-containing amorphous glass" (col. 3, lines 19-24) produced by Balcar et al.'s process is simply not porous.

Fusing the glass necessarily eliminates any possible porosity. Applicants include for the Examiner's reference an excerpt from the monograph, Glasses for Photonics (Cambridge University Press, ISBN 13:9780521580533) which includes a plot of viscosity as a function of temperature for a number of common commercial glasses (Fig. 1.4), including the soda lime glass referenced by Balcar et al. From the chart, it can be seen that fusing the glass at 1200 degrees C such as disclosed in Example 2 of Balcar et al. would result in a soda lime glass with a viscosity of about 10^3 dPas.s, comparable to molten polymers and the like. Any otherwise entrapped gas would quickly escape from a liquid with this low viscosity.

Thus, a process requiring preparing "a porous, inert base particle" such as independent claim 39, is not disclosed or suggested by Balcar et al. Similarly, a limitation specifying particles with porosity within a specific range, such as required by claims 41, 42 and 44, is not disclosed or suggested by Balcar et al. Likewise, the present dependent claims, which all incorporate the limitation of the claim(s) upon which they depend, require porous, inert base particles, and these are disclosed or suggested by Balcar et al. either.

Comminuting glass rod cannot make the glass porous. There is nothing in Balcar et al.'s disclosure that would teach or suggest to one of ordinary skill in the art that Balcar et al.'s process would result in a porous product.

In fact, the Examiner herself notes that Balcar et al.'s frit product, which includes toxic metals, meet current EPA standards for leachables for drinking water, that is, there is negligible leaching of the toxic metals from the frit. Balcar et al. disclose that the product is "insoluble" and "demonstrates no leaching of the hazardous waste" (col. 6, lines 22-25). One of ordinary skill in the art would understand from this description that Balcar et al.'s product would be completely useless for applicants' purposes.

Furthermore, Balcar et al. fail to teach, suggest or disclose the presently claimed process in that the stone chips in the present process are not fused. This is reflected by applicants' teaching that "[t]he porosity of the granule bodies can be controlled by selection of the shape and particle size distribution of the mineral particles provided" (page 8, lines 27-28), and claimed in new claims 46-50. If the stone chips were to melt, their shape and particle size distribution, which are physical characteristics of solid particles, would be entirely irrelevant to porosity. Further, applicants teach that "by selecting mineral particles that are known to pack poorly, porosity can be increased"

(page 8, lines 29-30). This is entirely contradictory of a process including the hypothetical step of fusing the stone particles.

In applicants' process, heat is applied to insolubilize the binder, the opposite of what occurs in Balcar et al.'s process, in which heat is used to melt the glass dust.

Balcar et al. teach away from the use of stone chips in their process. In particular, they teach the substitution of fusible glass dust for the stone dust that was previously employed to coat the inside of filter bags used to trap hazardous waste resulting from secondary aluminum smelting (col. 1, lines 25-43).

None of the secondary references cited by the Examiner make up for the fundamental deficiencies of the primary reference relied upon. Consequently, Balcar et al. taken with any one or any combination of Joedicke, Skadulis, and/or McMahon do not make out a *prima facie* case of obviousness. Thus, there is nothing which discloses or would suggest the presently claimed process to one of ordinary skill in the art.

Reconsideration and withdrawal of the rejection entered under 35 U.S.C. 103(a) of claims 4, 5, 7, 8, 13, 14 and 39-43 over Balcar et al. in view of Joedicke/Skadulis/McMahon are respectfully requested as applicable to the amended claims for these reasons.

Claims 9 - 12 and 44 - 45 stand rejected under 35 U.S.C. 103(a) as being unpatentable over Balcar et al in view of Joedicke/Skadulis, further in view of U.S. Patent 6,306,795 ("Ryan et al."). This rejection is also respectfully traversed, and reconsideration and withdrawal of the rejection are respectfully requested as applicable to the amended claims.

The Examiner states that she is applying Balcar et al. in view of Joedicke/Skadulis here for the same reasons as in the case of the initial rejection.

The Examiner notes that Balcar et al. in view of Joedicke/Skadulis fail to teach that an algacide-forming compound is dissolved in a fluid to form a solution, the solution being drawn into the pores in the base particles by capillary action to form solution-laden particles, the solution-laden particles being subsequently treated to convert the algacide-forming compound to an inorganic algacide (referencing claims 9, 11, 12, 44); the algacide-forming compound is a soluble copper salt (referencing claim 10).

The Examiner states that Ryan et al teach that cuprous oxide can be incorporated into a porous carrier material such as silica/alumina (referencing column 10, lines 27-28) by impregnating the porous carrier material with an aqueous solution of copper salts such as copper nitrate using, for example, the well known pore-volume impregnation (PVI) method (referencing column 11, lines 4-7, 22-42, 50-67), air drying and calcining the impregnated porous carrier material at 200 °C-540 °C to convert the copper salt to cupric oxide, cuprous oxide, or a mixture of the two (referencing column 12, lines 1-22).

The Examiner concludes that it would have been obvious to one of ordinary skill in the art at the time the invention was made to have added copper salts such as copper nitrate in an aqueous coating composition of Balcar et al in view of Joedicke/Skadulis instead of Cu_2O (which the Examiner identifies with the claimed slurry) before firing at 700 degrees F (371 °C) with the expectation of providing the desired intimate mixture of copper oxides with the porous carrier material since Ryan et al teach that cuprous oxide can be incorporated into a porous carrier material, such as silica/alumina by impregnating the porous carrier material with an aqueous solution of copper salts such as copper nitrate using, for example, the well-known pore-volume impregnation (PVI)

method, air drying and calcining the impregnated porous carrier material at 200 °C-540 °C to convert the copper salt to cupric oxide, cuprous oxide, or a mixture of the two.

Applicants respectfully contend that the cited combination of references does not make out a *prima facie* case of obviousness. As explained above, the comminuted waste glass resulting from Balcar et al.'s process is simply not porous. Therefore, the process disclosed by Ryan et al. can not be used to impregnate the waste glass with copper oxide. There is nothing in Ryan et al. or any combination of the cited references that would remedy this fundamental deficiency.

Reconsideration and withdrawal of the rejection of claims 9 - 12 and 44 - 45 over Balcar et al. in view of Joedicke/Skadulis and further in view of Ryan et al. as applicable to the amended claims are respectfully requested for this reason.

Claims 44-45 stand rejected under 35 U.S.C. 103(a) as being unpatentable over Balcar et al in view of Joedicke/Skadulis, further in view of U.S. Patent Publication 20030068303 ("Selvig et al."). This rejection is also respectfully traversed, and reconsideration and withdrawal of the rejection as applicable to the amended claims are respectfully requested.

First, it should be noted that Selvig et al. is not believed to be prior art with respect to the presently claimed invention, and applicants intend to submit evidence to that effect should the Examiner remain unpersuaded that even were Selvig et al. prior art, the combination of art cited in support of the present rejection does not make out a *prima facie* case of obviousness, and thus should be withdrawn.

The Examiner states that Balcar et al. in view of Joedicke/Skadulis are being applied here for the same reasons as discussed in relation to the initial rejection.

The Examiner notes that Balcar et al. in view of Joedicke/Skadulis fail to teach that inorganic algaecide is provided within the base particles (referencing claim 44).

The Examiner further states that Selvig et al. teach that a solid carrier such as mineral granules (referencing P91, P93) can be provided with inorganic chemical fungicides (referencing P25) such as cuprous oxide (referencing P54) either by impregnating pellets of the solid carrier with an active ingredient or by pelletizing a mixture of the active ingredient and powdered solid carrier (referencing P93). The Examiner also states that in other words, Selvig et al. teach that impregnating pellets of the solid carrier with an active ingredient is functionally equivalent to pelletizing a mixture of the active ingredient and powdered solid carrier.

The Examiner concludes that it would have been obvious to one of ordinary skill in the art at the time the invention was made to have pelletized glass dust together with cuprous oxide in Balcar et al. in view of Joedicke/Skadulis instead of coating preformed granules with a cuprous oxide-containing composition with the expectation of providing the desired algae-resistant roofing granules, since Selvig et al. teach that impregnating pellets of the solid carrier with an active ingredient is functionally equivalent to pelletizing a mixture of the active ingredient and powdered solid carrier.

The Examiner's conclusion is not correct. The cited group of references does not make out a *prima facie* case of obviousness with respect to either claim 44 or claim 45.

First, as explained above, Balcar et al. do not disclose porous or suggest "porous, inert base particles" such as required by independent claim 44. Neither Skadulis nor Joedicke remedy this fundamental deficiency.

Selvig et al. relates to environmentally compatible fungicide ("ECF") compositions that include chemical fungicides, "plus a biologic component that includes

microorganisms such as bacteria, yeast and fungi." (P. 21). According to the inventors, the "addition of a biologic component to the chemical fungicide(s) increases the efficacy and reduces the toxicity of the new compositions compared to chemical fungicides applied without the added microorganisms." Id.

The Examiner does not accurately state Selvig et al.'s disclosure at Paragraph 93, which is expressly stated to apply to the preparation of "dustable powders and granules," that is, powders or granules that have so little mechanical strength that they easily crumble into dust.

Further, the claim 44 requires "insolubilizing the binder by firing the base particles in a kiln at a temperature of at least 800 degrees C".

One of ordinary skill in the art would understand that a temperature of 800 degrees C would kill any "biologic component" in Selvig et al.'s compositions, and that thus Selvig et al. on the one hand and Joedicke and Skadulis on the other hand relate to incompatible and non-analogous arts.

Thus, the equivalence of pelletizing a mixture of an active ingredient and a powdered solid carrier with the impregnation of pellets of the solid carrier with an active ingredient drawn from Selvig et al.'s disclosure is necessarily limited to the agricultural fungicide art, and cannot be extended to the roofing granule art.

Even if the suggested equivalence could be extended to the roofing granule art, the presently cited combination of references would not make a *prima facie* case of obviousness. As noted above, Balcar et al. discloses fusing glass powder mixed with waste products, and comminuting the resulting product. The resulting material is not porous. The hazardous waste product does not leach out from the glass. Selvig et al.'s

teaching of equivalence, which is limited to the preparation of "dustable powders and granules," does not apply here.

Reconsideration and withdrawal of the rejection of claims 44 and 45 over Balcar et al in view of Joedicke/Skadulis, and further in view of Selvig et al., as applicable to the amended claims are respectfully requested for these reasons.

Applicants respectfully solicit reconsideration, withdrawal of the rejections entered, and an early notice of allowance.

July 13, 2006

Order No. 4104

Respectfully submitted,



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Glasses for Photonics

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Hardback (ISBN-13: 9780521580533 | ISBN-10: 0521580536)

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46 tables
Weight: 0.73 kg

Library of Congress

Dewey number: 621.36
Dewey version: 21
LC Classification: TA450 .Y36 2000
LC Subject headings:
Glass
Photonics--Materials

[Library of Congress Record](#)

This book is an introduction to recent progress in the development and application of glass with special photonics properties. Glasses have a number of structural and practical advantages over crystalline materials, including excellent homogeneity, variety of form and size, and the potential for doping with a variety of dopant materials. Glasses with photonic properties have great potential and are expected to play a significant role in the next generation of multimedia systems. Fundamentals of glass materials are explained in the first chapter, and the book then proceeds to a discussion of gradient index glass, laser glasses, nonlinear optical glasses and magneto-optical glasses. Beginning with the basic theory, the book discusses actual problems, performance and applications of glasses. The book will be of value to graduate students, researchers and professional engineers working in materials science, chemistry and physics with an interest in photonics and glass with special properties.

- First-ever comprehensive treatment of recent progress in the basic theory, actual problems, performance and applications of photonic glass materials
- Top notch authors

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Glass properties

Introduction

Glass can be made with excellent homogeneity in a variety of forms and sizes, from small fibers to meter-sized pieces. Furthermore, glass can be doped with rare earth ions and microcrystallites and a wide range of properties can be chosen to meet the needs of various applications. These advantages over crystalline materials are based on the unique structural and thermodynamic features of glass materials. Before discussing the special properties of glass, the fundamentals of glass materials are given in this chapter.

1.1 Features of glass as an industrial material

1.1.1 Structural features

1.1.1.1 Atomic arrangement

A glass is defined in ASTM [1] as ‘an inorganic product of fusion which has been cooled to a rigid condition without crystallization’. According to this definition, a glass is a noncrystalline material obtained by a melt-quenching process. Nowadays, noncrystalline materials that can not be distinguished from melt-quenched glasses of the same composition are obtainable by using various techniques such as chemical vapor deposition, sol-gel process, etc. Therefore, most glass scientists regard the term ‘glass’ as covering ‘all noncrystalline solids that show a glass transition’ regardless of their preparation method.

The words ‘noncrystalline solids’ and ‘glass transition’ suggest that a glass cannot be classified either in the category of crystalline materials such as quartz, sapphire, etc. or in the category of liquid. The atomic arrangement of a glass is different from those of crystalline materials and lacks long-range regularity, as schematically shown in Fig. 1.1 [2]. This is quite close to the

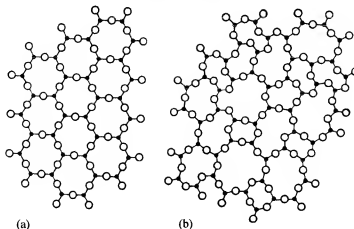


Fig. 1.1. Schematic two-dimensional illustration of the atomic arrangement in (a) crystal and (b) glass [2].

atomic arrangement in a liquid. There is neither crystal lattice nor lattice point in the glass structure and therefore, instead of diffraction peaks a halo is seen in the X-ray diffraction patterns of a glass.

Substances which can form noncrystalline solids with the atomic arrangement shown in Fig. 1.1(b) and at an appreciable size are found in oxide, halide, and chalcogenide systems. The three-dimensional random network of strong bonds is developed by the constituent called the 'network former'. Some components called network modifiers can also participate in glass formation by acting to modify the glass properties. These components do not form networks but occupy thermodynamically stable sites as illustrated schematically in Fig. 1.2 or act as a replacement for a part of 'network former'.

Glass formation is possible, in principle, for a system of any composition provided that it contains sufficient of the component called 'network former'. Thus, a wide variety of multi-component glasses can be prepared to attain the desired properties by adjusting the chemical composition at a level below 1%. The lack of regularity of the atomic arrangement over a long range, i.e. the randomness of the structure, is essential to the understanding of the physical and chemical features relevant to those glasses which have the special properties that will be reviewed in this book.

The local environment of the modifying ions in Fig. 1.2 is different from site to site because of the lack in regularity of structure. Since an active ion doped in a glass occupies a similar position to the modifier ions, the absorption and emission spectra from the ion, if any, are broader than those from active ions

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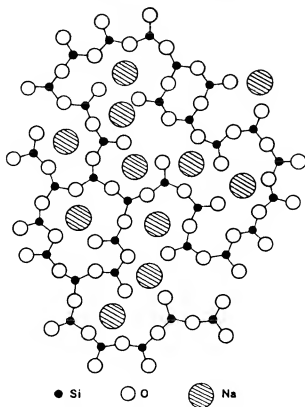


Fig. 1.2. Schematic two-dimensional illustration of the structure of a binary sodium silicate glass [3].

doped in a crystalline material as shown in Fig. 1.3 [4], a feature which is often advantageous in the preparation of a special glass.

The macroscopic properties of a glass such as optical transmission and absorption, refraction of light, thermal expansion, etc. are observed always equally in all directions, provided that the glass is free from stress and strain. That is, a glass is an isotropic material, whereas crystalline materials are generally anisotropic.

1.1.1.2 Chemical composition

Another important feature attributed to the uniqueness of the structure of glass is the flexibility of the chemical composition. Unlike crystalline materials, there is no requirement of stoichiometry among constituents provided that the electrical neutrality over the whole structure of a glass is maintained. Further-

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unique properties inherent to the doped elements such as special color, emission of fluorescent light, high nonlinear susceptibility, etc.

The other feature that comes from the flexibility of glass composition is the ability to modify the properties of a glass through ion-exchange [6]. There are many stable sites for network modifier ions in a glass structure as shown in Fig. 1.2. For example, alkali ions that are easily thermally activated can move from one stable site to another within a glass. Such a movement of alkali ions within a glass structure enables us to replace alkali ions near the surface of a glass by other ions of the same valence, i.e. Na^+ by K^+ ; Na^+ by Ag^+ ; K^+ by Tl^+ , etc. This replacement of alkali ions in the original glass by other ions partially modifies the composition of the glass, and hence its properties. The technique, which will be described later in detail, is particularly important for the modification of optical and mechanical properties.

1.1.2 Thermodynamic features

1.1.2.1 Glass transition

A glass whose atomic arrangement lacks regularity over a long range generally has higher configuration entropy, and hence higher free energy, than a crystalline material of the same composition. In other words, a glass is a thermodynamically metastable material which remains un-transformed to its most stable state due to hindrance of the atomic rearrangement during the process of glass formation. The transformation of a glass to a crystal proceeds via nucleation and crystal growth under the driving force of the difference in free energy between crystal and glass, ΔG_v , which increases with the increase of super cooling ΔT_r . Both nucleation rate I_0 and crystal growth rate U are dependent on the viscosity η of a super-cooled liquid as well as on ΔG_v .

Since the viscosity η increases exponentially with decreasing temperature as shown in Fig. 1.4 [7], the influence of viscosity on the hindrance of atomic rearrangement increases with decreasing temperature, whereas the driving force for the transformation into crystal increases with decreasing temperature.

Thus the nucleation rate I_0 and crystal growth rate U are approximately expressed by the following Eq. (1.2) and (1.3) [8, 9]:

$$I_0 = k_1/\eta \exp(-g\alpha^3\beta/T_r(\Delta T_r)^2) \quad (1.2)$$

where k_1 is a constant (typically about 10^{30} dyne cm), $T_r = T/T_m$, $\Delta T_r = (T_m - T)/T_m$, g is a factor related to the shape of the nucleus and equal to $16\pi/3$ for a spherical nucleus, and α and β are dimensionless parameters given by

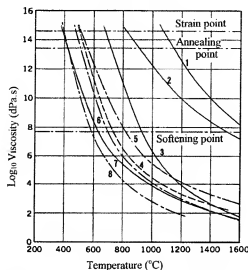


Fig. 1.4. Viscosity–temperature relationship of some commercial glasses. 1: Silicate glass; 2: High (96%) silica glass; 3: Aluminosilicate glass; 4: Soda-lime silicate glass (sheet glass); 5: Borosilicate glass; 6: Soda-lime silicate glass (electric bulb); 7: Lead-alkali silicate glass (electric use); 8: Lead-alkali silicate glass (high lead content). [7] [Reprinted from E. B. Shand, *Glass Engineering Handbook*, (McGraw-Hill Book Company, Inc., 1958) p. 16 copyright (1958) with permission from Corning Inc.]

$$\alpha = (N_A V_C^2)^{1/3} \sigma / \Delta H_{\text{IM}} \quad (1.2a)$$

and

$$\begin{aligned} \beta &= \Delta H_{\text{IM}} / RT_m \\ &= \Delta S_{\text{IM}} / R \end{aligned} \quad (1.2b)$$

where N_A is Avogadro's number, V_C is the molar volume of the crystal, σ is the crystal–liquid interface energy, ΔH_{IM} is the molar enthalpy of fusion and ΔS_{IM} is the molar entropy of fusion. For typical nonmetals, $\alpha\beta^{1/3}$ is about 0.5 ~ 0.7.

$$U = f(RT/3N_A\pi\lambda^2\eta)(1 - \exp[\Delta H_{\text{IM}}\Delta T/RTT_m]) \quad (1.3)$$

where f is the fraction of the site at which the glass-to-crystal transition can take place on the crystal surface and $\Delta T = T_m - T$, respectively.

In the temperature range near melting point T_m , the influence of $\Delta H_{\text{IM}}/T_m$ is predominant and, in the temperature range well below melting point, the influence of viscosity η is very large compared with the influence of $\Delta H_{\text{IM}}/T_m$. The schematic illustration of I_0 and U as a function of temperature gives curves which pass through maximum as shown in Fig. 1.5.

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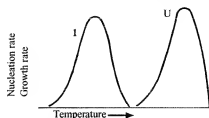


Fig. 1.5. Schematic illustration of temperature dependence of nucleation rate and crystal growth rate in a super-cooled liquid.

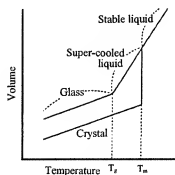


Fig. 1.6. Volume-temperature relationship of glass-forming liquid, and nonglass-forming liquid.

An important fact to be noted in the figure is that the temperature giving the maximum crystal growth rate (U) is higher than the one giving the maximum nucleation rate (I). When a viscous liquid is cooled from a high temperature, it passes through the temperature region of high crystal growth rate before nucleation takes place. When it passes through the temperature region of high nucleation rate, the crystal growth rate is already very low. Thus, a viscous liquid cooled at a sufficient rate further increases its viscosity to near or above 10^{14} dPa s without being transformed into a crystal. Once the viscosity reaches this value, even the alteration of the local atomic arrangement to equilibrate with temperature is not possible, resulting in the 'frozen-in' structure. Then the material behaves as a rigid and brittle solid, i.e. a glass. Physical and chemical phenomena occurring in a solid glass are no longer so sensitive to temperature change except for those that are enhanced by thermal activation such as the movement of alkali ions. Figure 1.6 shows the temperature dependence of the molar volume of a viscous super-cooled liquid, and uses glass as an example.

The transition from a viscous liquid to a solid glass is called the 'glass

transition' and the temperature corresponding to this transition is called the 'glass transition temperature', T_g . The reversible transformation from a glass to a viscous liquid also takes place if a glass is heated to a temperature above T_g .

Since the glass transition occurs as a result of the increase of viscosity and the rate of viscosity increase is dependent on cooling rate, the glass transition temperature, T_g , is not always the same even if the chemical composition is the same, but instead it is usually different, depending on the cooling rate of a liquid. A slow cooling allows enough time for a viscous liquid to alter its local atomic arrangement to attain the minimum free energy at the corresponding temperature, whereas a rapid cooling causes an increase of viscosity that is too quick for the local atomic arrangement to follow and results in a transition into a glass at a higher temperature.

The structure of a rapidly cooled glass is more open than that of a slowly cooled one because the 'freezing-in' of the atomic arrangement occurs at a higher temperature. The properties of a glass are therefore different from glasses to glass, depending on the thermal history, even if the chemical composition is the same.

1.1.2.2 Thermal stability and structural relaxation

A glass obtained by cooling a liquid can transform into a crystal if re-heated to a temperature region that is well above T_g , where the nucleation and crystal growth takes place. Figure 1.7 shows an example of the crystallization of a glass detected by a differential thermal analysis (DTA) [10]. The exothermic peak observed in the temperature near 700 °C is attributed to crystallization. The sharpness of the peak and the difference between onset temperature and T_g reflect the thermal stability of a glass. If a glass is thermally unstable, the exothermic peak is sharp and the temperature difference is small.

On the other hand, if the temperature of re-heating is not high and remains near the glass transition temperature, which is well below the temperature giving high crystal growth rate, a glass remains uncrystallized but undergoes some change in atomic arrangement called structural relaxation [11]. The differences in structure and properties between glasses of different thermal history can be eliminated by the structural relaxation brought about by this heat treatment near the glass transition temperature. Figure 1.8 shows an example of such a change attributed to the structural relaxation [12]. It should be noted from this figure that the tuning of some properties of glass is possible by holding the glass at a temperature near the transition temperature.

1.1 Glass as an industrial material

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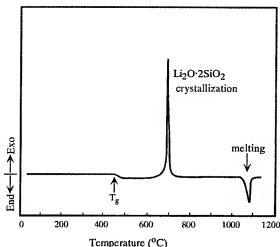


Fig. 1.7. Differential thermal analysis curve of $\text{Li}_2\text{O}-\text{SiO}_2$ glass heated at a rate of $10^\circ\text{C min}^{-1}$ [10].

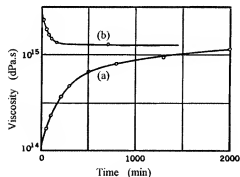


Fig. 1.8. Viscosity-time curves of a soda-lime silica glass at 486.7°C [12]. (a) Newly drawn fiber; (b) Fiber stabilized at 477.8°C for 64 h.

1.1.3 Optical features

1.1.3.1 Transparency

There is neither grain boundary nor interface within a glass structure and so the intrinsic scattering loss of a glass is very small. Therefore, a glass is, in principle, transparent to light in the wavelength region where the intrinsic absorption does not occur, i.e. between two intrinsic absorption edges determined by band-gap energy and the vibration energy of constituents.

Glasses of oxide and fluoride systems that have a wide gap between the conduction and valence bands are generally transparent to light in the visible